449. *Aromatic Fluoro-compounds. Part I. Synthesis of 2,4,6-Trinitrobenzotrifluoride.*

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2,4,6-Trinitrobenzotrifluoride has been prepared by conversion of the known 3-hydroxy-2,4,6-trinitrobenzotrifluoride into 3-chloro-2,4,6-trinitrobenzotrifluoride followed by reduction. In general, 2,4,6-trinitrobenzotrifluoride forms molecular addition compounds in the same manner as 2,4,6-trinitrotoluene.

Direct ordinary nitration of benzotrifluoride gives only the *m*-nitro-derivative,[1] or under more drastic conditions 3,5-dinitrobenzotrifluoride.[2] In attempting to prepare 2,4,6-trinitrobenzotrifluoride two routes were investigated. It was contemplated that 2,4,6-trinitrobenzotrichloride could be prepared by Ganguly's method [3] and converted into the corresponding trifluoro-material by metathetical exchange with anhydrous hydrogen fluoride. However, in a number of attempts, Ganguly's work could not be repeated. Jones [4] has prepared both *o*- and *p*-nitrobenzotrifluoride and VanderWerf *et al.*[5] has nitrated 3-acetamidobenzotrifluoride to obtain 5-acetamido-2-nitrobenzotrifluoride a and tetranitro-derivative of 3-acetamidobenzotrifluoride.

The only reference to a clean, symmetrical trinitration of a substituted benzotrifluoride is Whalley's preparation [6] of 3-hydroxy-2,4,6-trinitrobenzotrifluoride from 3-hydroxybenzotrifluoride which contains the strongly *ortho-para*-orienting hydroxyl group.

3-Hydroxy-2,4,6-trinitrobenzotrifluoride is converted *via* its pyridine salt into the 3-chloro-derivative with phosphorus oxychloride.[7] This method is a marked improvement over the classic method, wherein phosphorus pentachloride is used, without a solvent, which gives rise to large quantities of intractable materials.[8]

It was thought that 3-chloro-2,4,6-trinitrobenzotrifluoride could be easily reduced with copper powder and ethanol–water by a method similar to that used for the preparation of 1,3,5-trinitrobenzene from picryl chloride.[9] However, under these conditions the starting material was recovered quantitatively. The chloride was, however, reduced by sodium iodide–acetic acid in acetone.[10]

In contrast to the very ready nitration of *m*-hydroxybenzotrifluoride, under similar conditions *o*-nitro- and *m*-chloro-benzotrifluoride yielded no nitration products, the trifluoromethyl group being hydrolysed as reported by LeFave.[11] In a similar fashion 2,4,6-trinitrobenzotrifluoride yielded 1,3,5-trinitrobenzene, decarboxylation following hydrolysis of the trifluoromethyl group.

Experimental

m-*Hydroxybenzotrifluoride*.—This compound was prepared by diazotization and subsequent hydrolysis of *m*-aminobenzotrifluoride. After steam-distillation the material had b. p. 55—57°/3 mm., n_D^{25} 1·4572. Carpenter *et al.*[12] give n_D^{25} 1·4570.

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[2] Finger and Reed, *J. Amer. Chem. Soc.*, 1944, **66**, 1952.
[3] Ganguly, *Ber.*, 1925, **58**, 708.
[4] Jones, *J. Amer. Chem. Soc.*, 1947, **69**, 2346.
[5] VanderWerf, Helin, and Sveinbjornsson, *J. Amer. Chem. Soc.*, 1951, **73**, 1189.
[6] Whalley, *J.* 1950 2592.
[7] Boyer, Spencer, and Wright *Canad. J. Res.* 1946 **24**, *B*, 200.
[8] Jackson and Gazzolo, *Amer. Chem. J.*, 1900, **23**, 376.
[9] Desvenques, *Chim. et Ind.*, 1931, **25**, 291.
[10] Blatt and Tristram, *J. Amer. Chem. Soc.*, 1952, **74**, 6273.
[11] LeFave, *J. Amer. Chem. Soc.*, 1949, **71**, 4148.
[12] Carpenter, Easter, and Wood, *J. Org. Chem.*, 1951, **16**, 586

3-*Hydroxy*-2,4,6-*trinitrobenzotrifluoride*.—*m*-Hydroxybenzotrifluoride (60 g.) was dropped into nitric acid (180 ml.) at the rate of 20 drops per min. at room temperature without cooling. Nitrogen oxides were evolved. Near the end of the addition the product began to crystallize. Next a mixture of fuming acid (10 ml.) and concentrated sulphuric acid (40 ml.) was added and stirring continued for another hour. The whole was then poured on ice and the solids were filtered off. After drying in air the compound was recrystallized by adding hexane to its alcoholic solution, to give pale yellow crystals (81%), m. p. 122—123° (Whalley [6] reports 122°) (Found: C, 28·4; H, 0·6. Calc. for $C_7H_2F_3N_3O_6$: C, 28·3; H, 0·7%).

Pyridine Salt of 3-*Hydroxy*-2,4,6-*trinitrobenzotrifluoride*.—Pyridine (7·9 g., 0·1 mole) was added to 3-hydroxy-2,4,6-trinitrobenzotrifluoride (29·7 g., 0·1 mole) in 95% alcohol (200 ml.). The salt was precipitated as large yellow crystals, m. p. 179—180°. Whalley [6] reports 179°.

3-*Chloro*-2,4,6-*trinitrobenzotrifluoride*.—The pyridine salt (37·6 g., 0·1 mole) was suspended in sodium-dried benzene (50 ml.) to which phosphorus oxychloride (15·3 g., 0·1 mole) was then added. After 2 hours' refluxing the now homogeneous solution was washed with cold water and evaporated, to give a slightly yellow solid. Recrystallization from 95% alcohol yielded the *chloro-compound* as white needles (28·0 g., 89%), m. p. 89—90° [Found: C, 26·8; H, 0·62; N, 13·2; Cl, 11·3; F, 18·0%; *M* (Rast), 309. $C_7HClF_3N_3O_6$ requires C, 26·6; H, 0·3; N, 13·3; Cl, 11·2; F, 18·6%; *M*, 315].

2,4,6-*Trinitrobenzotrifluoride*.—The 3-chloro-compound (20 g.) was dissolved in dry acetone (40 ml.) and added to sodium iodide (24 g.) and glacial acetic acid (8 ml.) in dry acetone (80 ml.), and the whole was refluxed for 3 hr., then cooled and poured into cold aqueous sodium sulphite (10 g. in 200 ml.), a brown oil being precipitated. The water–acetone layer was decanted and crushed ice (50 g.) was added to the oil. After several minutes' stirring the oil solidified and was dissolved in hot 95% alcohol. Crystallization occurred after addition of several drops of water and the crystals were filtered off. After drying under a vacuum at room temperature for 6 hr., the material was recrystallized from benzene three times, to yield white crystals (16·2 g., 92%), m. p. 88·5—89° (negative Beilstein test) [Found: C, 30·1; H, 1·1; N, 14·9; F, 19·1%; *M* (Rast), 276. Calc. for $C_7H_2F_3N_3O_6$: C, 29·9; H, 0·7; N, 14·9; F, 20·3%; *M*, 281].

Hydrolysis of 2,4,6-*Trinitrobenzotrifluoride*.—2,4,6-Trinitrobenzotrifluoride (2 g.) and concentrated sulphuric acid (15 ml.) were sealed in a tube cooled in solid carbon dioxide and acetone, then heated at 250° for 72 hr. Pouring the product on ice gave plates which, recrystallized from 95% alcohol, melted at 60—61° and so correspond to the α-form of 1,3,5-trinitrobenzene. A sample recrystallized with an equal amount of authentic 1,3,5-trinitrobenzene melted at 120·0—120·5° which corresponds to the β-form.

Molecular Addition Compounds of 2,4,6-*Trinitrobenzotrifluoride*.—Addition compounds with the following were prepared from 0·01 mole each of the amine and 2,4,6-trinitrobenzotrifluoride in alcohol and allowing the compound to crystallize: *N*-methylaniline, m. p. 56—57°, violet needles; α-naphthylamine, m. p. 110°, violet needles; aniline, m. p. 80—81°, dark red needles; *o*-phenylenediamine, m. p. 85—86°, dark red needles.

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